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CHEMICAL NOTES.

BY GEORGE HAY.

I. *On the Decomposition of Stannous Chloride in a Geissler Tube.*

While observing, in company with my friend, Dr. Wm. M. Herron, the spectrum of chloride of tin through a powerful spectroscope of four prisms (Browing's make)—the Geissler's spectrum-tube used for the purpose being illuminated by the spark from a large Ruhmkorff's coil connected to six cells and a Leyden jar and a tin foil condenser, the spark being capable of passing six inches in air—the following facts were noted :—

The constricted portion of the tube became hot—the spectrum became gradually feebler and feebler and ultimately ceased—a vacuum had formed within the tube so perfect that the spark would not pass.

On examining the tube I found a metallic deposit or mirror of extreme thinness, but having the well-known metallic lustre deposited upon the glass at the negative end. The wire inside of the tube at the positive end was tarnished, and had lost its metallic lustre, and was covered with a white though thin incrustation. I too hastily concluded that this was anhydrous proto-chloride of platinum, and thank Dr. Koenig for his communication correcting me, as shall appear anon. I had no time just then to investigate further—hence the mistake.

I have used up the tube in making the following observations :—

Before opening the tube I heated the end containing the mirror and found that it did not sublime.

Cut off the tube half an inch above the film, and noticed that the wire within the tube at this end was fused to a globule of the size of a pin-head adhering to the glass projecting within the tube, through which the wire passed.

Introduced one drop of concentrated hydrochloric acid, and, upon spreading this drop over the film and slightly warming, the film dissolved completely.

Rinsed out the solution with water into a small evaporating basin, and evaporated to a few drops, to concentrate as much as possible and remove the large excess of acid.

Treated one drop in a watch glass with hydrosulphuric acid, and got a few brownish-yellow flakes soluble in potash. Treated another drop in a watch glass with hydrosulphuric acid, and introduced fluid and flakes into a narrow tube closed at one end, and evaporated in an air bath—heated this, but only a little free sulphur sublimed, leaving a few grayish flakes in the bottom of the tube. Chased back the sulphur to the bottom of the tube, and covered it and the minute flakes with powdered dry ferrocyanide of potassium and heated again, but, as might have been expected from former experiment upon original mirror, got no mirror anew. Treated another drop with nitric acid, and got upon evaporation the slightest observable white film insoluble in nitric acid. Chloride of mercury yielded a white opalescence. The quantity of metal was so exceedingly small that, had I not experimented upon single drops, I should have got nothing in the way of a reaction. I got no reaction with gold, owing to the extreme minuteness of the quantity of metal. I do not believe that I could have weighed the quantity of metal composing this delicate mirror, but I did not attempt it. It must be remembered that all the chloride of tin within the tube originally was only a vacuum of its vapor ; but it yielded the spectrum of chloride of tin, and it is well known that the spectroscope will yield certain results where ordinary chemical tests fail altogether.

The tarnished wire at the other end of the tube was not fused.

Scraped off a little of the tarnish with a penknife blade into a small watch glass and added one drop of water, but the flakes did not dissolve.

To make sure whether the drop of water mentioned had dissolved any chloride, added a small drop of nitrate of silver solution, but obtained no opalescence.

Scraped off the whole of the white tarnish and digested with a few drops of strong hydrochloric acid, and got thus a clear solution. One drop of this solution treated with hydrosulphuric acid gave no precipitate. Another drop treated with ammonia yielded a few gelatinous-looking flakes soluble in caustic potassa.

This white substance, therefore, appeared to be alumina, but, as in the case of the metal, there was extremely little of it—it had probably been chloride of aluminium, and, with the residual air or perhaps some moisture in the tube, had been converted into the oxide at the high temperature produced by the spark, a temperature sufficiently high to fuse the wire at the other end under the protecting influence of the mirror already mentioned. *Within* the tube at this end I found the wire consisted of aluminium, and *outside* of the tube at the same end it consisted of platinum, which had, I suppose, been joined to the aluminium by fusion. The tin salt was undoubtedly decomposed by electrolysis even when existing as an attenuated vapor.

II. *On the Solubility of Tin, Arsenic, and Antimony in concentrated Nitric Hydrate at* 36° *F.*

The following facts have never, so far as I am aware, been published, either by myself or by any one else. I have already communicated to the Academy that the metal tin is soluble in a mixture of pure concentrated nitric acid and water in equal volumes. What I have now to communicate is, that tin forms with the undiluted acid a soluble salt, viz. the proto-nitrate of tin.

The circumstances under which the salt was formed were as follows: Into a dry test-tube I poured a small quantity of pure concentrated nitric acid, and then set the tube containing the acid afloat in a vessel of water at a temperature of 36° F. Into the acid I dropped a fragment of pure tin; it became coated with a white substance, and in the course of fifteen minutes was entirely transformed into this white substance. Several fragments of tin were added at the above intervals, and all were transformed into this white subtance. The action of the acid had now become less decided, although the fluid was still strongly acid, and the contents of the tube presented a gelatinous appearance resembling the recently precipitated hydrate of alumina. It seemed doubtful whether I had not merely obtained the ordinary hydrate of metastannic acid. Upon the addition of about two volumes of water the whole of the white substance dissolved to a clear and colorless fluid, therefore holding the tin in the solution and proving that the white substance was not the hydrate of metastannic acid.

The solution was tested as follows :—

1st. A portion was boiled and the whole of the dissolved metal was precipitated as hydrate of metastannic acid.

2d. After neutralizing a portion of the free acid, hydrosulphuric acid caused the precipitation of proto-sulphide of tin mixed with sulphur.

3d. To a portion of the original solution was added solution of chloride of mercury, and in the course of a few hours a white precipitate formed consisting of sub-chloride of mercury.

4th. Chloride of gold gave no precipitate.

5th. Potash solution gave a white precipitate soluble in excess of potash.

6th. A mixture of ferricyanide of potassium and sesquichloride of iron was made, and to this mixture was added a portion of the original solution—the result was the production in a few hours of prussian blue.

These tests were, in my opinion, retarded by the presence of a large excess of nitric acid, and the production of purple of Cassius was altogether prevented by the presence of an excess of this acid. All the other tests were perfectly satisfactory.

To obviate the difficulty occasioned by the presence of a large excess of free nitric acid, a fresh solution was prepared by adding the metal to the acid until the contents of the tube had become thick and pasty, and there appeared to be little or no action going on, the tube being kept, as before, surrounded by water at 36° F.

Water was now added to the pasty mass, but in this instance a not very considerable portion of white substance was left undissolved. The solution was filtered, and to the clear filtrate was added—

1st. Hydrosulphuric acid. This yielded a brown precipitate soluble in solution of potash, and reprecipitated brown on addition of dilute hydrochloric acid.

2d. Potash yielded a white precipitate soluble in excess of potash.

3d. Chloride of gold yielded a beautiful and strong coloration of purple of Cassius after addition of a drop of dilute hydrochloric acid in five minutes, and when the tin solution was not too dilute the purple of Cassius was precipitated at once.

4th. Chloride of mercury yielded a white precipitate of sub-chloride of mercury immediately.

5th. To a mixture of ferricyanide of potassium and sesquichloride of iron, a portion of the clear filtrate was added, and almost immediately prussian blue was formed.

6th. Boiling the original filtrate caused the precipitation of the tin as hydrate of metastannic acid.

The above experiments prove that not only is tin converted into a soluble salt by concentrated nitric acid, but that proto-nitrate of tin is formed.

Pursuing my investigations still further with regard to the action of nitric acid upon the group of metals usually said to be oxidized, but not dissolved or converted into salts by it, I next experimented upon antimony.

Into a dry test-tube I poured about 2 c.c. of concentrated nitric acid, and then dropped into the acid about 20 grains of powdered antimony. The tube was immediately set afloat in a vessel of water at 36° F. and allowed to remain for about 12 hours, being shaken occasionally to diffuse the powder through the acid. At first there appeared to be no change produced, but by and by the fluid became distinctly green, and by the end of 12 hours a strongly green solution was obtained. On decanting this green fluid from the powdered metal and diluting it with water, a bulky and abundant white precipitate was produced, showing that a large proportion of the antimony had been dissolved in the nitric acid, and in this respect it appeared to behave like nitrate of bismuth when diluted with water. In order to ascertain in what state of combination the antimony was held, the following experiments were made.

Tartaric acid was added to the fluid containing the precipitate, and it at once dissolved to a colorless fluid.

The fluid was now filtered in order to remove any particles of undissolved metal which might have been decanted.

1st. After neutralizing a portion of the free acid in a portion of the filtrate, a strong solution of hydrosulphuric acid was added —the result was a bulky, orange-red, unmistakable precipitate of tersulphide of antimony, readily soluble in potash, and reprecipitated from its alkaline solution by dilute hydrochloric acid.

2d. To another portion of the filtrate, potash was added, and a white precipitate of teroxide of antimony was obtained soluble in excess.

3d. To the alkaline solution last obtained, nitrate of silver was added, and there was obtained a jet-black precipitate of suboxide of silver insoluble in excess of ammonia—this being distinctive of *ter*oxide of antimony.

4th. Neutralized another portion of original filtrate by ammonia to remove free nitric acid, and then acidulated with hydrochloric acid. Put a drop or two of the solution thus obtained upon a clean surface of platinum, and introduced a fragment of zinc—the result was a dark-brown or black stain of metallic antimony not removable by cold hydrochloric acid, but removable by hot nitric acid.

These four tests show that the original solution contained teroxide of antimony, and, as the solution was obtained by means of nitric acid, the probability is that it was a ternitrate of antimony, for a *large quantity* of the metal was dissolved. The HS precipitate was so bulky as at first almost to fill the test-tube.

The solution of antimony in *nitric acid kept cold* will not bear dilution with water except in presence of tartaric or hydrochloric acid.

Boiling the original green solution gave an abundant white precipitate of antimonic acid accompanied by copious evolution of orange-red fumes. Boiled till the red fumes had disappeared—diluted and filtered—the filtrate did not pass through clear, but on passing twice more through the same filter was obtained a perfectly clear filtrate. This filtrate gave every one of the four tests above-mentioned with the utmost readiness, *i. e.*, it yielded in succession tersulphide of antimony, teroxide of antimony, suboxide of silver, and metallic antimony, and therefore held in solution even after formation and precipitation of antimonic acid by boiling a *large quantity* of teroxide of antimony dissolved in nitric acid, or existing as ternitrate of antimony. In this case no other acid but the nitric had been used.

I now experimented upon arsenic in the same manner, *i. e.*, by keeping the pure metal (not pulverized) for 12 hours in contact with pure concentrated nitric acid at 36° F.

The result was a beautiful transparent green solution of the entire quantity of metal. This solution yielded every one of the tests for arsenic acid.

1st. After reduction by sulphurous acid and partial neutralization, it yielded upon addition of hydrosulphuric acid the tersulphide of arsenic.

2d. After complete neutralization, and addition of sulphide of ammonium, followed by addition of hydrochloric acid, it yielded the pentasulphide of arsenic.

3d. After addition of nitrate of silver and a small quantity of ammonia, it yielded the reddish-brown precipitate of arsenate of silver.

4th. In similar circumstances, *i. e.*, after neutralization by ammonia and addition of sulphate of copper, it yielded the greenish-blue precipitate of arsenate of copper.

5th. Neutralized and then mixed with a *large* excess of concentrated hydrochloric acid and boiled with a slip of clean copper, a dark-gray film was deposited on the metal.

6th. Neutralized and added a clear mixture of sulphate of magnesia, chloride of ammonium and ammonia, it yielded at once a crystalline precipitate of arsenate of ammonia and magnesia. The original green solution was therefore either simple arsenic acid or a pentanitrate of arsenic.

The curious fact is here observed that these three metals, arsenic, antimony, and tin, when treated with cold concentrated nitric acid *kept* cold, oxidized in the relation of their several volatilities—arsenic yielding either a *penta*nitrate? or merely arsenic acid, antimony yielding a *ter*nitrate, and tin a *proto*nitrate; while the other curious fact is also to be observed that on boiling the original solutions *all* the arsenic remains in solution, a *considerable portion* of the antimony remains in solution, and *none* or only the merest trace of the tin remains in solution.

I ought to have mentioned in my last communication that the tin employed was not granulated but only cut by a sharp knife from a bar in order to prevent too rapid action of the acid upon the metal. I found it necessary on the other hand, to pulverize the antimony, as without this the action was hardly visible—the arsenic was used in large crystals.

Note upon Mr. Hay's Paper. By Geo. A. Koenig, Ph.D.

The reaction of nitric hydrate upon arsenic at 36° F. results, according to the author, in the exclusive formation of arsenic acid or arsenic pentoxide. This is not substantiated by his experiments. He certainly proved the presence of the pentoxide, but does not speak of any test for the teroxide, the presence of which does not interfere much with the other reactions. It is a fact well known by chemists, that a continued digestion of the teroxide is needed with concentrated nitric acid to change it into pentoxide, and some authors state distinctly that arsenic is changed by nitric acid both into the teroxide and pentoxide.

Since it is known that by the action of nitric acid upon metals heat is generated, and also that antimony and tin are precipitated by heat from their nitric or other acid solutions, it was not astonishing to find those metals go into and remain in solution, by abstracting the heat with a cooling liquid in such measure as heat was generated.

In the case of tin, dilute nitric acid is known to dissolve it as protoxide, and here the water in the acid prevents the heating; in using concentrated acid and applying a cooling liquid at the outside of the vessel, the conditions remain unchanged, and only the application is different.